



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



Publication number:

**0 571 906 A2**

**EUROPEAN PATENT APPLICATION**

Application number: 93108295.2

Int. Cl.<sup>5</sup>: G03C 1/498, G03C 7/02,  
B41M 5/28

Date of filing: 21.05.93

Priority: 22.05.92 US 887778

Date of publication of application:  
01.12.93 Bulletin 93/48

Designated Contracting States:  
DE FR GB IT

Applicant: MINNESOTA MINING AND  
MANUFACTURING COMPANY  
3M Center,  
P.O. Box 33427  
St. Paul, Minnesota 55133-3427(US)

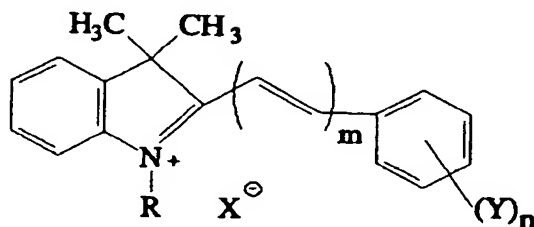
Inventor: Helland, Randall H., c/o Minnesota  
Mining and  
Manufac. Company,  
2501 Hudson Road,  
P.O. Box 33427

St. Paul, Minnesota 55133-3427(US)  
Inventor: Tiers, George V. D., c/o Minnesota  
Mining and  
Manufac. Company,  
2501 Hudson Road,  
P.O. Box 33427  
St. Paul, Minnesota 55133-3427(US)  
Inventor: Stevenson, Dian E., c/o Minnesota  
Mining and  
Manufac. Company,  
2501 Hudson Road,  
P.O. Box 33427  
St. Paul, Minnesota 55133-3427(US)

Representative: VOSSIUS & PARTNER  
Postfach 86 07 67  
D-81634 München (DE)

Thermal dye bleach construction.

A thermal-dye-bleach construction comprising a thermal nucleophile-generating agent in association with a styryl dye having a nucleus of general formula (I):



representing the nucleus of a styryl dye in which

- R = methyl or ethyl group  
Y = alkoxy of 1 to 20 carbon atoms  
m = 1 or 2,  
n = 1, 2, or 3, and  
X<sup>o</sup> = an anion

The aromatic fused benzene portion of the indolenine ring may be further substituted with commonly acceptable dye substituents such as alkyl and substituted alkyl (of 1 to 10 carbon atoms) groups, alkoxy groups (preferably of 1 to 10 carbon atoms), fused aromatic rings (as to make the benzene ring a fused naphthalene ring), halogen

(including fluoro), cyano, nitro, carboxamido, amido, etc. One or two substituents chosen variously from said group may also be present on the phenyl ring to which the alkoxy group is attached. These substituents and their combinations should not be chosen so as to alter the absorption characteristics of the dye greatly enough to remove the maximum absorption from between 300 and 490 nm.

X<sup>e</sup> may be any anion, but certain classes of anions and certain particular anions are preferred. Aromatic and perfluorinated anions and, in particular dodecylbenzenesulfonate and especially perfluoro(ethylcyclohexane sulfonate) are preferred on account of their solubilizing power, but simpler anions such as iodide, chloride, bromide, methylsulfate, perchlorate and the like may also be used.

This invention relates to a thermal-dye-bleach system and in particular to a thermal-dye-bleach system comprising a narrow class of styryl dyes and a thermal nucleophile generating agent, and the use of the system in photographic materials.

The increasing availability and use of focused or laser light sources and particularly lasers which emit in the ultraviolet and blue region of the electromagnetic spectrum has led to a need for high quality photographic materials which are sensitive in this region, especially from 300 nm to 490 nm.

In order to improve the image sharpness of photographic materials it is customary to incorporate a dye in one or more layers of the material, the purpose of which is to absorb light that has been scattered within the coating and would otherwise lead to reduced image sharpness. Dyes used for this purpose are known as antihalation dyes if incorporated in a separate backing layer or underlayer and as acutance dyes if incorporated into the light sensitive layer itself.

It is usually essential that antihalation or acutance dyes should completely decolorize under the processing conditions of the photographic material concerned. In the case of photothermographic materials which are processed by simply heating for a short period of time at temperatures usually between 100°C and 200°C, any antihalation or acutance dyes used must decolorize thermally.

Various thermal-dye-bleach systems are known in the prior art including single compounds which spontaneously decompose and decolorize at elevated temperature and combinations of dye and thermal dye bleaching agent which together form a thermal-dye-bleach system.

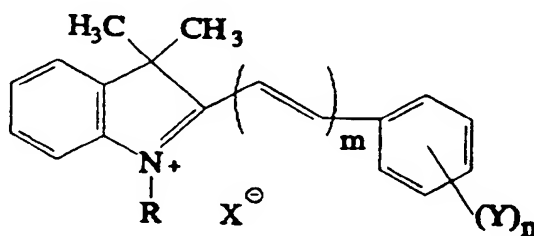
U.S. Patent Nos. 3,609,360, 3,619,194, 3,627,527, 3,684,552, 3,852,093, 4,033,948, 4,088,497, 4,196,002, 4,197,131, 4,201,590 and 4,283,487 disclose various thermal-dye-bleach systems which absorb principally in the visible region of the electromagnetic spectrum and the near-infrared region.

A variety of thermal base-generating agents are known and have been used in photothermographic materials. However, in most cases in which thermal base-releasing agents have been incorporated into photothermographic constructions in the prior art, the purpose has been to increase the alkalinity of the medium during thermal processing and to promote the development reaction. Thermal base-releasing agents have been used thus in photothermographic materials of both the diazo type and silver based materials.

Patent 4,370,401 uses nitrate salts to bleach dyes of a different structure than the dyes of this invention, but including at least one styryl dye. Also it was found that bleaching of this nitrate system was seriously inhibited in the cellulose-acetate-butyrate binder system required to achieve acceptable adhesion to polyester.

It has now been found that certain (blue-absorbing) yellow and UV-absorbing alkoxy substituted styryl dyes will substantially or completely bleach upon heating in the presence of thermal nucleophile-generating agents.

According to the present invention there is provided a thermal-dye-bleach construction comprising a thermal nucleophile-generating agent in association with a class of alkoxy styryl dyes having a nucleus of general formula (I):



representing the nucleus of a styryl dye in which

- R = alkyl groups of 1 to 20 and preferably 1 to 5 carbon atoms such as methyl or ethyl group,
- Y = alkoxy of 1 to 20 carbon atoms, preferably of 1 to 10 carbon atoms,
- m = 1 or 2,
- n = 1, 2, or 3, and
- X<sup>-</sup> = an anion

The aromatic fused benzene portion of the indolenine ring system may be further substituted with commonly acceptable dye substituents such as alkyl and substituted alkyl groups (of 1 to 10 carbon atoms), alkoxy groups (preferably of 1 to 10 carbon atoms), fused aromatic rings (as to make the benzene ring a fused naphthalene ring), halogen (including fluoro), cyano, nitro, carboxamido or amido. One or two

acid and analyzing about 14.5 percent silver, represents a preferred example. Transparent sheet materials made on transparent film backing require a transparent coating and for this purpose the silver behenate "full soap", containing not more than about four or five percent of free behenic acid and analyzing about 25.2 percent silver may be used.

The method used for making silver soap dispersions is well known in the art and is disclosed in Research Disclosure April 1983 (22812), *ibid* October 1983 (23419), and U.S. Patent No. 3,985,565.

The light-sensitive silver halide used in the present invention can be employed in a range of 0.0005 mol to 1.0 mol and, preferably, from 0.005 mol to 0.2 mol, and more preferably from 0.008 to 0.15 mol per mol of organic silver salt.

The silver halide may be any photosensitive silver halide such as silver bromide, silver iodide, silver chloride, silver bromiodide, silver chlorobromiodide or silver chlorobromide.

The silver halide used in the present invention may be employed without modification. However, it may be chemically sensitized with a chemical sensitizing agent such as a compound containing sulfur, selenium or tellurium or a compound containing gold, platinum, palladium, rhodium or iridium, a reducing agent such as a tin halide, or a combination thereof. The details of these procedures are described in T.H. James "The Theory of the Photographic Process", Fourth Edition, Chapter 5, pages 149 to 169.

The silver halide may be added to the emulsion layer in any fashion which places it in catalytic proximity to the aforementioned organic silver salt.

The silver halide and the organic silver salt which are separately formed in a binder may be mixed prior to use to prepare a coating solution, but it is also effective to blend both of them in a ball mill for a period of time. Further, it is effective to use a process which comprises adding a halogen-containing compound to the prepared organic silver salt to partially convert the silver of the organic silver salt to silver halide.

Methods of preparing these silver halide and organic silver salts and manners of blending them are described in Research Disclosure No. 170-29, Japanese Patent Applications Nos. 32928/75 and 42529/76, U.S. Patent No. 3,700,458, and Japanese Patent Applications Nos. 13224/74 and 17216/75.

The preformed silver halide emulsions of this invention can be "unwashed" or washed to remove soluble salts. In the latter case the soluble salts can be removed by leaching or the emulsion can be coagulation washed, e.g., by the procedures described in Hewitson, et al., U.S. Patent No. 2,618,556; Yutzy et al., U.S. Patent No. 2,614,928; Yackel, U.S. Patent No. 2,565,418; Hart et al., U.S. Patent No. 3,241,969; and Waller et al., U.S. Patent No. 2,489,341. The silver halide grains may have any crystalline habit including, but not limited to cubic, tetrahedral, orthorhombic, tabular, laminar or platelet.

Photothermographic emulsions containing preformed silver halide in accordance with this invention can be sensitized with chemical sensitizers, such as with reducing agents; sulfur, selenium or tellurium compounds; gold, platinum or palladium compounds, or combinations of these. Suitable chemical sensitization procedures are described in Shepard, U.S. Patent No. 1,623,499; Waller, U.S. Patent No. 2,399,083; McVeigh, U.S. Patent No. 3,297,447; and Dunn, U.S. Patent No. 3,297,446.

The light-sensitive silver halides can be spectrally sensitized with various known dyes including cyanine, styryl, hemicyanine, oxonol, hemioxonol and xanthene dyes. Useful cyanine dyes include those having a basic nucleus, such as a thiazoline nucleus, an oxazoline nucleus, a pyrroline nucleus, a pyridine nucleus, an oxazole nucleus, a thiazole nucleus, a selenazole nucleus and an imidazole nucleus. Useful merocyanine dyes which are preferred include those having not only the above described basic nuclei but also acid groups, such as a thiohydantoin nucleus, a rhodanine nucleus, an oxazolidinedione nucleus, a thiazolidinedione nucleus, a barbituric acid nucleus, a thiazolinone nucleus, a malononitrile moiety and a pyrazolone nucleus. In the above described cyanine and merocyanine dyes, those having imino groups or carboxyl groups are particularly effective. Practically, the sensitizing dye to be used in the present invention is properly selected from known dyes as described in U.S. Patent No. 3,761,279, 3,719,495 and 3,877,943, British Patent Nos. 1,466,201, 1,469,117 and 1,422,057, Japanese Patent Application (OPI) Nos. 27924/76 and 156424/75, and so on, and can be located in the vicinity of the photocatalyst according to known methods used in the above-described examples. These spectral sensitizing dyes are used in amounts of about  $10^{-4}$  mol to about 0.1 mol per 1 mol of photocatalyst.

The reducing agent for silver ion may be any material, preferably organic material, which will upon silver metal catalysis reduce silver ion to metallic silver. Conventional photographic developers such as phenidone, hydroquinones, and catechol are useful but hindered phenol reducing agents are preferred. The reducing agent should be present as 1 to 10 percent by weight of the imaging layer. In a two-layer construction, if the reducing agent is in the second layer, slightly higher proportions, of from about 2 to 15 percent tend to be more desirable.

A wide range of reducing agents have been disclosed in dry silver systems including amidoximes such as phenylamidoxime, 2-thienylamidoxime and p-phenoxyphenylamidoxime, azine, e.g., 4-hydroxy-3,5-

dimethoxybenzaldehyde azine; a combination of aliphatic carboxylic acid aryl hydrazides and ascorbic acid, such as 2,2-bis(hydroxymethyl)propionyl-beta-phenyl hydrazide in combination with ascorbic acid; a combination of polyhydroxybenzene and hydroxylamine, a reductone and/or a hydrazine, e.g., a combination of hydroquinone and bis(ethoxyethyl)hydroxylamine, piperidinohexose reductone or formyl-4-methylphenyl hydrazine, hydroxamic acids such as phenylhydroxamic acid, p-hydroxyphenyl hydroxamic acid, and beta-alanine hydroxamic acid; a combination of azines and sulfonamidophenols, e.g., phenothiazine and 2,6-dichloro-4-benzenesulfonamidophenol; alpha-cyanophenylacetic acid derivatives such as ethyl-alpha-cyano-2-methylphenylacetate, ethyl alpha-cyanophenylacetate; bis-beta-naphthols as illustrated by 2,2'-dihydroxy-1,1'-binaphthyl, 6,6'-dibromo-2,2'-dihydroxy-1,1'-binaphthyl, and bis(2-hydroxy-1-naphthyl)methane; a combination of bis-beta-naphthol and a 1,3-dihydroxybenzene derivative, e.g., 2,4-dihydroxybenzophenone or 2'4'-dihydroxyacetophenone; 5-pyrazolones such as 3-methyl-1-phenyl-5-pyrazolone; reductones as illustrated by dimethylamino hexose reductone, anhydro dihydro amino hexose reductone, and anhydro dihydro piperidone hexose reductone; sulfonamido-phenol reducing agents such as 2,6-dichloro-4-benzenesulfonamidophenol, and p-benzenesulfonamidophenol; 2-phenylindane-1,3-dione and the like; chromans such as 2,2-dimethyl-7-t-butyl-6-hydroxychroman; 1,4-dihydro-pyridines such as 2,6-dimethoxy-3,5-dicarbetoxy-1,4-dihydropyridine; bisphenols e.g., bis(2-hydroxy-3-t-butyl-5-methylphenyl)methane, 2,2-bis(4-hydroxy-3-methylphenyl)propane, 4,4-ethylidenebis(2-tert-butyl-6-methylphenol), and 2,2-bis(3,5-dimethyl-4-hydroxyphenyl)propane; ascorbic acid derivatives, e.g., 1-ascorbylpalmitate, ascorbylstearate and unsaturated aldehydes and ketones, such as benzyl and diacetyl; 3-pyrazolidones and certain indane-1,3-diones.

The literature discloses additives, "toners", which improve the image.

Toner materials may be present, for example, in amounts from 0.1 to 10 percent by weight of all silver bearing components. Toners are well known materials in the photothermographic art as shown in U.S. Patent Nos. 3,080,254; 3,847,612 and 4,123,282.

Examples of toners include phthalimide and N-hydroxyphthalimide; cyclic imides such as succinimide, pyrazoline-5-ones, and a quinazolinone, 3-phenyl-2-pyrazoline-5-one, 1-phenylurazole, quinazoline, and 2,4-thiazolidinedione; naphthalimides, e.g., N-hydroxy-1,8-naphthalimide; cobalt complexes, e.g., cobaltic hexamine trifluoroacetate; mercaptans as illustrated by 3-mercapto-1,2,4-triazole, 2,4-dimercaptopyrimidine, 3-mercapto-4,5-diphenyl-1,2,4-triazole and 2,5-dimercapto-1,3,4-thiadiazole; N-(aminomethyl)aryl dicarboximides, e.g. (N-dimethylaminomethyl)-phthalimide, and N-(dimethylaminomethyl)naphthalene-2,3-dicarboximide; and a combination of blocked pyrazoles, isothiuronium derivatives and certain photobleach agents, e.g., a combination of N,N'-hexamethylene bis(l-carbamoyl-3,5-dimethylpyrazole), 1,8-(3,6-diazaoctane)bis(isothiuronium trifluoroacetate) and 2-(tribromomethylsulfonyl)-benzothiazole; and merocyanine dyes such as 3-ethyl-5[(3-ethyl-2-benzothiazolinyldiene)-1-methylethylidene]-2-thio-2,4-oxazolidinedione; phthalazinone, phthalazinone derivatives or metal salts or these derivatives such as 4-(1-naphthyl)-phthalazinone, 6-chlorophthalazinone, 5,7-dimethoxyphthalazinone, and 2,3-dihydro-1,4-phthalazinedione; a combination of phthalazinone plus phthalic acid derivatives, e.g., phthalic acid, 4-methylphthalic acid, 4-nitrophthalic acid, and tetrachlorophthalic anhydride; quinazolinones, benzoxazine or naphthoxazine derivatives; rhodium complexes functioning not only as tone modifiers but also as sources of halide ion for silver halide formation in situ, such as ammonium hexachlororhodate (III), rhodium bromide, rhodium nitrate and potassium hexachlororhodate (III); inorganic peroxides and persulfates, e.g., ammonium peroxydisulfate and hydrogen peroxide; benzoxazine-2,4-diones such as 1,3-benzoxazine-2,4-dione, 8-methyl-1,3-benzoxazine-2,4-dione, and 6-nitro-1,3-benzoxazine-2,4-dione; pyrimidines and asym-triazines, e.g., 2,4-dihydroxypyrimidine, 2-hydroxy-4-aminopyrimidine, and azauracil, and tetrazapentalene derivatives, e.g., 3,6-dimercapto-1,4-diphenyl-1H,4H-2,3a,5,6a-tetrazapentalene, and 1,4-di(o-chloro-phenyl)3,6-dimercapto-1H,4H-2,3a,5,6a-tetrazapentalene.

A number of methods have been proposed for obtaining color images with dry silver systems. Such methods include incorporated coupler materials, e.g., a combination of silver benzotriazole, well known magenta, yellow and cyan dye-forming couplers, aminophenol developing agents, a base release agent such as guanidinium trichloroacetate, and silver bromide in poly(vinyl butyral); a combination of silver bromide, sulfonamidophenol reducing agent, silver behenate, poly(vinyl butyral), an amine such as n-octadecylamine and "2-equivalent" or "4-equivalent" cyan, magenta or yellow dye-forming couplers; incorporating leuco dye bases which oxidize to form a dye image, e.g., the leuco forms of Malachite Green, Crystal Violet and pararosaniline; a combination of in situ silver halide, silver behenate, 3-methyl-1-phenylpyrazolone and N,N'-dimethyl-p-phenylenediamine hydrochloride; incorporating phenolic leuco dye reducing agents such as 2-(3,5-di-tert-butyl-4-hydroxyphenyl)-4,5-diphenylimidazole, and bis(3,5-di-tert-butyl-4-hydroxyphenyl)phenylmethane; incorporating azomethine dyes or azo dye reducing agents; a silver dye bleach process, e.g., an element comprising silver behenate, behenic acid, poly(vinyl butyral), poly(vinyl-butylal)peptized silver bromide emulsion, 2,6-dichloro-4-benzene sulfonamido phenol, 1,8-(3,6-

diazaoctane)bis-isothiuronium-p-toluene sulfonate and an azo dye, was exposed and heat processed to obtain a negative silver image with a uniform distribution of dye, which was laminated to an acid activator sheet comprising polyacrylic acid, thiourea and p-toluene sulfonic acid and heated to obtain well defined positive dye images; and incorporating amines such as aminoacetanilide (yellow dye-forming), 3,3'-dimethoxybenzidine (blue dye-forming) or sulfanililide (magenta dye forming) which react with the oxidized form of incorporated reducing agents such as 2,6-dichloro-4-benzene-sulfonamido-phenol to form dye images. Neutral dye images can be obtained by the addition of amines such as behenylamine and p-anisidine.

Leuco dye oxidation in such silver halide systems is disclosed in U.S. Patent Nos. 4,021,240, 4,374,821, 4,460,681 and 4,883,747.

Silver halide emulsions containing the stabilizers of this invention can be protected further against the additional production of fog and can be stabilized against loss of sensitivity during keeping. Suitable anti-foggants and stabilizers which can be used alone or in combination, include the thiazolium salts described in Staud, U.S. Patent No. 2,131,038 and Allen U.S. Patent No. 2,694,716; the azaindenes described in Piper, U.S. Patent No. 2,886,437 and Heimbach, U.S. Patent No. 2,444,605; the mercury salts described in Allen U.S. Patent No. 2,728,663; the urazoles described in Anderson, U.S. Patent No. 3,287,135; the sulfocatechols described in Kennard, U.S. Patent No. 3,235,652; the oximes described in Carrol et. al., British Patent No. 623,448; nitron; nitroindazoles; the polyvalent metal salts described in Jones, U.S. Patent No. 2,839,405; the thiuronium salts described by Herz, U.S. Patent No. 3,220,839; and palladium, platinum and gold salts described in Trivelli, U.S. Patent No. 2,566,263 and Damschroder, U.S. Patent No. 2,597,915.

Stabilized emulsions of the invention can contain plasticizers and lubricants such as polyalcohols, e.g., glycerin and diols of the type described in Milton, U.S. Patent No. 2,960,404; fatty acids or esters such as those described in Robins, U.S. Patent No. 2,588,765 and Duane, U.S. Patent No. 3,121,060; and silicone resins such as those described in DuPont British Patent No. 955,061.

The photothermographic elements can include image dye stabilizers. Such image dye stabilizers are illustrated by U.K. Patent No. 1,326,889; Lestina et al. U.S. Patent Nos. 3,432,300 and 3,698,909; Stern et al. U.S. Patent No. 3,574,627; Brannock et al. U.S. Patent No. 3,573,050; Arai et al. U.S. Patent No. 3,764,337 and Smith et al. U.S. Patent No. 4,042,394.

Photothermographic elements containing emulsion layers stabilized according to the present invention can be used in photographic elements which contain light absorbing materials and filter dyes such as those described in Sawdey, U.S. Patent No. 3,253,921; Gaspar U.S. Patent No. 2,274,782; Carroll et al., U.S. Patent No. 2,527,583 and Van Campen, U.S. Patent No. 2,956,879. If desired, the dyes can be mordanted, for example, as described in Milton and Jones, U.S. Patent No. 3,282,699.

Photothermographic elements containing emulsion layers stabilized as described herein can contain matting agents such as starch, titanium dioxide, zinc oxide, silica, polymeric beads including beads of the type described in Jelley et al., U.S. Patent No. 2,992,101 and Lynn, U.S. Patent No. 2,701,245.

Emulsions stabilized in accordance with this invention can be used in photothermographic elements which contain antistatic or conducting layers, such as layers that comprise soluble salts, e.g., nitrates, etc., evaporated metal layers, ionic polymers such as those described in Minsk, U.S. Patent Nos. 2,861,056, and 3,206,312 or insoluble inorganic salts such as those described in Trevoy, U.S. Patent No. 3,428,451.

The binder may be selected from any of the well-known natural or synthetic resins such as gelatin, polyvinyl acetals, polyvinyl chloride, polyvinyl acetate, cellulose acetate, polyolefins, polyesters, polystyrene, polyacrylonitrile, polycarbonates, and the like. Copolymers and terpolymers are of course included in these definitions. The preferred photothermographic silver-containing polymer is polyvinyl butyral, but ethyl cellulose, methacrylate copolymers, maleic anhydride ester copolymers, polystyrene, and butadiene-styrene copolymers may be used.

Optionally these polymers may be used in combination of two or more thereof. Such a polymer is used in an amount sufficient to carry the components dispersed therein, that is, within the effective range of the action as the binder. The effective range can be appropriately determined by one skilled in the art. As a guide in the case of carrying at least an organic silver salt, it can be said that a preferable ratio of the binder to the organic silver salt ranges from 15:1 to 1:2, and particularly from 8:1 to 1:1.

Photothermographic emulsions containing antihalation materials of the invention can be coated on a wide variety of supports. Typical supports include polyester film, "subbed" polyester film, poly(ethylene terephthalate) film, cellulose nitrate film, cellulose ester film, poly(vinyl acetal) film, polycarbonate film and related or resinous materials, as well as glass, paper, metal, and the like. Typically, a flexible support is employed, especially a paper support, which can be partially acetylated or coated with baryta and/or an alpha-olefin polymer, particularly a polymer of an alpha-olefin containing 2 to 4 carbon atoms such as polyethylene, polypropylene, ethylenebutene copolymers and the like.

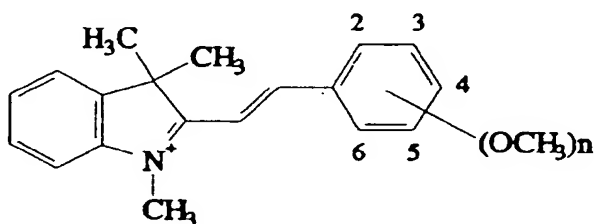
The substrate with backside resistive heating layer may also be used in color photothermographic imaging systems such as shown in U.S. Patent. Nos. 4,460,681 and 4,374,921.

Photothermographic emulsions of this invention can be coated by various coating procedures including dip coating, air knife coating, curtain coating, or extrusion coating using hoppers of the type described in Benguin, U.S. Patent No. 2,681,294. If desired, two or more layers may be coated simultaneously by the procedures described in Russell, U.S. Patent No. 2,761,791 and Wynn, British Patent No. 837,095.

The present invention will now be illustrated in detail in reference to the following examples, but the embodiment of the present invention is not limited thereto.

## EXAMPLES

In the following examples, dyes having two or three methoxy substituents on a common nucleus are shown. The common nucleus is



and the dyes in experimental examples will be defined by the position of attachment of the methoxy groups to the phenyl ring such as "2,4,5" indicating a 2,4,5-trimethoxyphenyl group. The anion in all cases was perfluoro(ethylcyclohexanesulfonate). This anion is also referred to herein as "PECHS."

### Examples 1 - 12

Typical heat bleachable antihalation formulations were prepared as described below and in Table II.

**Solution A:** A solution of Eastman cellulose acetate butyrate (CAB 381-20), Goodyear polyester (PE-200), 2-butanone, toluene, and 4-methyl-2-pentanone was prepared. To this was added *p*-nitrophenylsulfonylacetic acid where indicated (as in Experiments No. 7-12).

**Solution B:** A solution of methoxy substituted styryl dye in methanol was prepared.

**Solution C:** A solution of guanidine *p*-nitrophenylsulfonylacetate salt (thermal amine generator), methanol, dimethylformamide was prepared.

The resulting polymer, dye, and amine generator solutions were combined and mixed thoroughly and coated onto a polyester base using a knife coater. The wet coating thickness was 3 mil (76  $\mu$ m). The coating was dried 4 minutes at 180°F (82°C). The base can be a clear or white opaque polyester. On opaque polyester the following absorbances were obtained using a Hitachi reflectance mode spectrometer. Examples 1-6 contained no acid stabilizer. Examples 7-12 contained an acid stabilizer.

**TABLE I**

Examples 1-6 (Without Acid)

Expt. No.	Dye	Dmax	wavelength nm
1	3,4,5-	0.52	425
2	2,4-	0.78	450
3	2,3-	0.40	390
4	3,4-	0.72	445
5	2,4,5-	0.77	487
6	2,4,6-	1.09	460

Examples 7-12 (With Acid)

Expt. No.	Dye	Dmax	wavelength nm
7	3,4,5-	0.90	425
8	2,4-	1.48	450
9	2,3-	0.90	390
10	3,4-	1.20	445
11	2,4,5-	1.10	487
12	2,4,6-	1.40	460

The constructions were run through a 3M Model 9014 Dry Silver Processor. The temperature was 265°F (165°C) and dwell time was 10 seconds. All dye constructions completely bleached to an absorbance of 0.0. The results, shown below, indicate that acid-containing constructions have a higher  $D_{max}$  than the non-acid-containing constructions. This is due to improved "pot life" and resistance to bleaching during oven drying.

Aging studies were carried out by storing samples at 80°F (27°C) and 80% humidity and periodically measuring absorbance. Reflectance measurements of absorbance of samples of Examples 2 and 8 gave the following results:

Time	Example 2 Absorbance	Example 8 Absorbance
0	0.78	1.48
1 week	0.27	
2 weeks	0.06	0.36



**Table II - Typical Antihalation Formulation**

<u>Material</u>	<u>Without Acid wt. g</u>	<u>With Acid wt. g</u>
<u>Solution A:</u>		
Eastman Cellulose Acetate Butyrate (CAB)	0.4420	0.4420
Goodyear PE-200 Polyester	0.0059	0.0059
2-butanone	2.9637	2.9637
Toluene	1.4410	1.4410
4-methyl-2-pentanone	0.4830	0.4830
p-nitrophenylsulfonyl acetic acid (Acid) for dimethoxy dyes	0.0000	0.0121
p-nitrophenylsulfonyl acetic acid (Acid) for trimethoxy dyes	0.0000	0.0126
<u>Solution B:</u>		
Dye	0.0434	0.0434
Methanol	1.5500	1.5500
<u>Solution C:</u>		
Guanidine p-nitrophenylsulfonyl acetic acid salt - C <sub>1</sub> A <sub>1</sub> - (for dimethoxy dyes)	0.0584	0.0584
Guanidine p-nitrophenylsulfonyl acetic acid salt - C <sub>1</sub> A <sub>1</sub> - (for trimethoxy dyes)	0.0606	0.0606
Methanol	2.4000	2.4000
Dimethylformamide (DMF)	2.4000	2.4000

Example 13

Heat bleachable coatings with proportions similar to those of Example 2 may be prepared as follows:

A solution of Eastman cellulose acetate butyrate (CAB 381-20), Goodyear polyester (PE-200), 2-butanone, toluene, and 4-methyl-2-pentanone is prepared. To this is added p-nitrophenylsulfonylacetic acid.

A solution of methoxy substituted styryl dye in methanol is prepared.

A solution of thermal nucleophile generator salt (thermal amine generator) C<sub>1</sub>-C<sub>5</sub>; A<sub>1</sub>-A<sub>6</sub>, methanol and dimethylformamide, is prepared.

The resulting polymer, dye, and amine generator solutions are combined and mixed thoroughly and coated onto a polyester substrate using a knife coater. The wet coating thickness is 3 mil (76  $\mu$ m). The coating is dried 4 minutes at 180 °F (82 °C). The base is a clear or white opaque polyester.

The constructions are run through a 3M Model 9014 Dry Silver Processor. The temperature is 265°F (165°C) and dwell time is 10 seconds. All dye constructions would bleach.

#### Examples 14 and 15

These Examples describe the use of the coating of Example 8 as potential thermographic medium. The coating prepared as described in Experiment 8 had a strong yellow color.

In order to test the construction as a thermographic imaging material, the material was overcoated with 5% cellulose acetate solution in acetone (50 μm wet thickness). This coating prevented sticking and toner pick-off from an original.

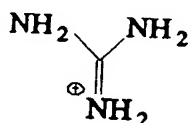
This coating was found to produce a pleasing negative clear-on- yellow transparent copy from printed text using a 3M Thermofax™ copier set at 2/3 maximum setting.

A sheet of the yellow coating prepared in Experiment 8 was also evaluated as a positive thermographic imaging material. An electronic signal was used to drive the thermal head of an Oyo Geo Space GS-612 Thermal Plotter to bleach the construction in the background areas. A positive yellow image on a clear background resulted.

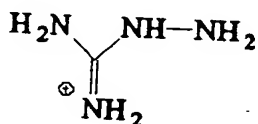
**TABLE III - Thermal Base Generating Salts**

#### Cations

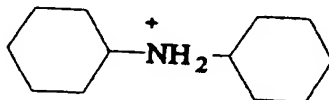
C<sub>1</sub>

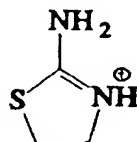
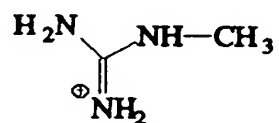
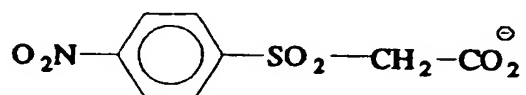
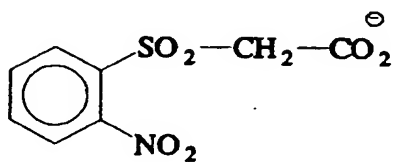
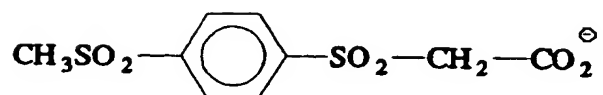


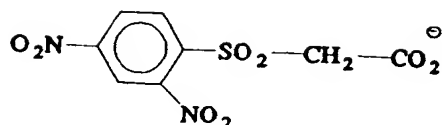
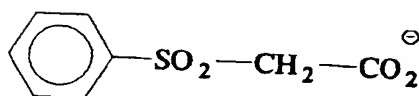
C<sub>2</sub>



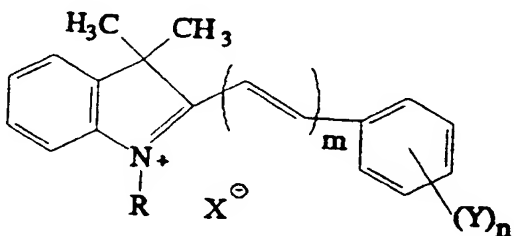
C<sub>3</sub>



CationsC<sub>4</sub>C<sub>5</sub>AnionsA<sub>1</sub>A<sub>2</sub>A<sub>3</sub>

AnionsA<sub>4</sub>A<sub>5</sub>A<sub>6</sub>Claims

1. A thermal-dye-bleach construction comprising a thermal nucleophile-generating agent in association with a styryl dye having a nucleus of general formula (I):



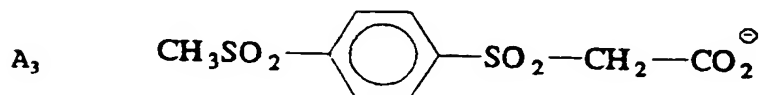
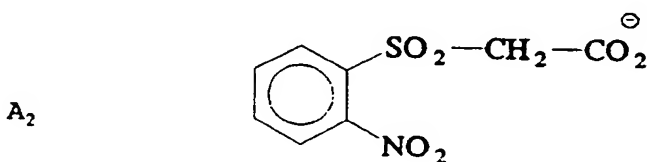
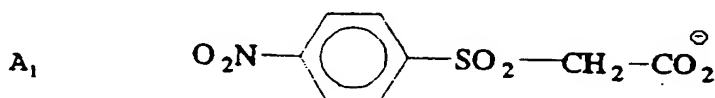
representing the nucleus of a styryl dye in which

- R = alkyl group of 1 to 20 carbon atoms,  
 Y = alkoxy of 1 to 10 carbon atoms,  
 m = 1 or 2,  
 n = 1, 2, or 3, and  
 X<sup>⊖</sup> = an anion.

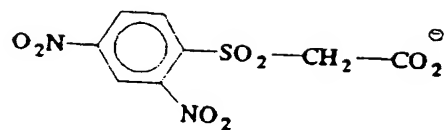
2. A thermal-dye-bleach construction as claimed in Claim 1 in which the thermal nucleophile-generating agent is a thermal amine-release agent.
3. A thermal-dye-bleach construction as claimed in Claim 2 in which the thermal amine-release agent comprises an amine salt of an organic acid which liberates one or more free amine groups upon thermal decomposition.

4. A thermal-dye-bleach construction as claimed in anyone of Claims 1 to 3 in the form of a photothermographic element comprising a support bearing an electromagnetic radiation sensitive photographic silver halide material, the element comprising as an antihalation or acutance agent the thermal nucleophile-generating agent and styryl dye.
5. A thermal-dye-bleach construction as claimed in Claim 4 in which the silver halide is primarily ultraviolet radiation sensitive.
6. A thermal-dye-bleach construction as claimed in Claim 4 or 5 in which the antihalation layer contains the styryl dye in an amount to provide a transmission optical density of at least 0.1 at the  $\lambda$  max of the dye.
7. A thermal-dye-bleach construction as claimed in anyone of Claims 4 to 6 in which the styryl dye is present in an amount in the range from 0.1 to 1.0 mg/dm<sup>2</sup>.
8. A thermal-dye-bleach construction as claimed in anyone of Claims 4 to 7 in which the photographic silver halide material is a photothermographic medium comprising one or two layers comprising silver halide in catalytic proximity to a light-insensitive silver salt, a binder, and a reducing agent for silver ion.
9. A thermal-dye-bleach construction as claimed in anyone of Claims 1 to 8 which further comprises an acid.
10. A thermal-dye bleach construction as claimed in Claim 9 in which the acid is the product derived from acidification of the anions selected from A<sub>1</sub> to A<sub>6</sub>:

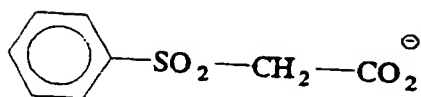
### Anions



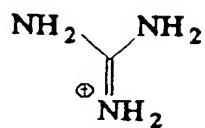
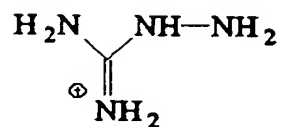
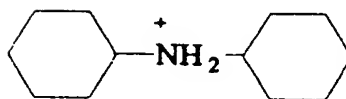
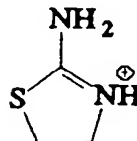
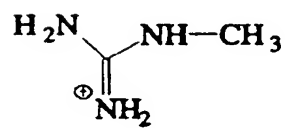
A<sub>5</sub>



A<sub>6</sub>



11. A thermal-dye-bleach construction as claimed in anyone of Claims 1 to 10 which further comprises a phenylsulfonyl acetic acid.
12. A thermal-dye-bleach construction as claimed Claims 2 to 11 in which the thermal-amine release agent comprises a thermal amine-generating salt comprising a cation selected from C1 to C5 in combination with an anion selected from A1 to A6 as described in Claim 10:

CationC<sub>1</sub>C<sub>2</sub>C<sub>3</sub>C<sub>4</sub>C<sub>5</sub>





(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) Publication number:

**0 571 906 A3**

(12)

**EUROPEAN PATENT APPLICATION**

(21) Application number: 93108295.2

(51) Int. Cl.<sup>5</sup>: **G03C 1/498, G03C 7/02, B41M 5/28**

(22) Date of filing: 21.05.93

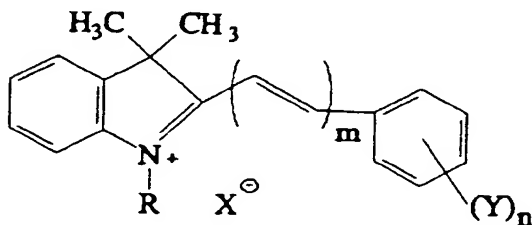
(30) Priority: 22.05.92 US 887778

(43) Date of publication of application:  
01.12.93 Bulletin 93/48(84) Designated Contracting States:  
DE FR GB IT(86) Date of deferred publication of the search report:  
13.07.94 Bulletin 94/28(71) Applicant: **MINNESOTA MINING AND MANUFACTURING COMPANY**  
3M Center,  
P.O. Box 33427  
St. Paul, Minnesota 55133-3427(US)(72) Inventor: **Helland, Randall H., c/o Minnesota Mining and Manufac. Company,**

2501 Hudson Road,  
P.O. Box 33427  
St. Paul, Minnesota 55133-3427(US)  
Inventor: Tiers, George V. D., c/o Minnesota Mining and Manufac. Company,  
2501 Hudson Road,  
P.O. Box 33427  
St. Paul, Minnesota 55133-3427(US)  
Inventor: Stevenson, Dian E., c/o Minnesota Mining and Manufac. Company,  
2501 Hudson Road,  
P.O. Box 33427  
St. Paul, Minnesota 55133-3427(US)

(74) Representative: **VOSSIUS & PARTNER**  
Postfach 86 07 67  
D-81634 München (DE)(54) **Thermal dye bleach construction.**

(57) A thermal-dye-bleach construction comprising a thermal nucleophile-generating agent in association with a styryl dye having a nucleus of general formula (I):



representing the nucleus of a styryl dye in which

- R = methyl or ethyl group  
Y = alkoxy of 1 to 20 carbon atoms  
m = 1 or 2,  
n = 1, 2, or 3, and

$x^{\ominus}$  = an anion

The aromatic fused benzene portion of the indolenine ring may be further substituted with commonly acceptable dye substituents such as alkyl and substituted alkyl (of 1 to 10 carbon atoms) groups, alkoxy groups (preferably of 1 to 10 carbon atoms), fused aromatic rings (as to make the benzene ring a fused naphthalene ring), halogen (including fluoro), cyano, nitro, carboxamido, amido, etc. One or two substituents chosen variously from said group may also be present on the phenyl ring to which the alkoxy group is attached. These substituents and their combinations should not be chosen so as to alter the absorption characteristics of the dye greatly enough to remove the maximum absorption from between 300 and 490 nm.

$x^{\ominus}$  may be any anion, but certain classes of anions and certain particular anions are preferred. Aromatic and perfluorinated anions and, in particular dodecylbenzenesulfonate and especially perfluoro-

(ethylcyclohexane sulfonate) are preferred on account of their solubilizing power, but simpler anions such as iodide, chloride, bromide, methylsulfate, perchlorate and the like may also be used.



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 93 10 8295

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
A	RESEARCH DISCLOSURE vol. 170, no. 40 , June 1978 , HAVANT GB pages 40 - 41 Y. S. YAMAMOTO ET AL 'ANTIHALATION MATERIALS FOR PHOTOTHERMOGRAPH' * Whole Article *	1-12	G03C1/498 G03C7/02 B41M5/28
A	US-A-3 481 927 (D. W. HESELTINE ET AL.) 2 December 1969 * column 2, line 18 - column 3, line 27 *	1-12	
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			G03C B41M
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 26 April 1994	Examiner Markowski, V
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03.92 (P04C01)

